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# WEAR RESISTANCE OF α- AND β- GALLIUM OXIDE COATINGS

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**Abstract**. Mechanical wear resistance of the α- and β- $Ga_2O_3$ polymorphs is experimentally studied. We report about tribological cyclic tests of these wide-band-gap semiconductor crystals. To the best of our knowledge, this is the first attempt at considering these crystals as protective coatings. The crystalline layers were deposited on sapphire substrates by vapour-phase epitaxy. This method allows applying coatings on large areas and surfaces of complex shapes, including the surfaces of a number of metals. It has been revealed, that both polymorphs are highly wear-resistant, and suddenly have a very low coefficient of friction. The α- $Ga_2O_3$ layers with the corundum structure exhibit wear coefficient values commensurate with those of sapphire and gallium nitride.

**Keywords:** gallium oxide, protective coatings, tribology, coefficient of friction, COF, wear resistance

## 1. Introduction

The Gallium Oxide ($Ga_2O_3$) is a novel functional crystal, firstly considered as a promising semiconductor material for electronic and sensor devices [1-3]. The $Ga_2O_3$ demonstrates a polymorphism – it has five crystalline modifications [1,2]. Of particular interest are the corundum-like rhombohedral α-phase and thermally stabile monoclinic β-phase [3,4]. By now it is known, that both polymorphs have relatively high mechanical properties (hardness, Young modulus, etc.) [5,6]. Also, there is an intimation that exists, that $Ga_2O_3$ may have high tribological characteristics [7]. Gallium oxide layers can be synthesized using a number of methods among which Halide Vapour Phase Epitaxy (HVPE) is one of the most common [8,9]. This technique allows obtaining high-quality $Ga_2O_3$ layers on complex surfaces with large areas [10,11]. All of the above potentiates to consider this material as a promising protective coating for various purposes, including the main tribological function – to protect machines and tools against an abrasion.

Close crystal kinship of α-$Ga_2O_3$ to sapphire (α-$Al_2O_3$) which has outstanding tribological characteristics [12-14] looks also attractive for experiments. In particular, the coefficient of friction (COF) for sapphire tested by sapphire probe within the tribological test is 0.2 [12,13]. The wear coefficient for sapphire tested by the diamond probe in the single scratch experiment is $10^{-6}$ $mm^3/(N \cdot m)$ [14].

In this paper behaviour of the α- and β-$Ga_2O_3$ epitaxial layers on sapphire substrates under friction is investigated.

## 2. Materials and Methods

The $Ga_2O_3$ layers were grown by HVPE technique by Perfect Crystals LLC. For the investigation specimens containing α- and β gallium oxide polymorphs were used. $Ga_2O_3$

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layers were deposited on the single crystalline $Al_2O_3$ substrates with basic (0001) orientation at ~ 500°C with obtaining the α-phase and at ~ 1000°C with obtaining the β-phase [10,11]. The α- and β-$Ga_2O_3$ layers were (0001) and $(\bar{2}01)$ faced respectively. The sapphire was chosen as a substrate due to the fact that both $Ga_2O_3$ layers synthesized at sapphire had far better morphology, than the ones synthesized at metal or ceramic. Such layers can be used as-grown without additional treatment in a model experiment.

The tribological tests were performed by a microtribometer running in the reciprocating test with the dry slip mode using the "sphere-on-plane" model with a variable probe load. The cross-sections located perpendicular to the wear tracks were recorded by a profilometer. A Scanning Electron Microscopy (SEM) was applied to analyze the wear tracks geometry. The thicknesses of the α- and β-$Ga_2O_3$ layers (measured by the layer cleavage using SEM) were of an order of 5 μm and 4 μm, respectively. The roughness of the $Ga_2O_3$ layers (determined by the profilometer) had the values of $R_a$=0.046 / 0.198 (α- / β-phase), $R_z$=0.243 / 1.537 (α- / β-phase), where $R_a$ is an arithmetic average height and $R_z$ is a ten-point height [15]. The tests were carried out under standard atmospheric conditions (ISA): room temperature, normal atmospheric pressure, 40% relative humidity (RH). When all tests were completed, no significant contrbody wear was found, which was confirmed by SEM. Using data received by the tribological tests and the profilometer measurements, the wear tracks widths, the COF ($\mu$) values, and the wear coefficients ($k$) were calculated.

## 3. Results and discussion

The tribological tests were performed using a 100Cr6 steel ball contrbody of 4mm diameter. The reciprocating test amplitude (half of the full cycle length) was 6 mm, the total run-length was 50 m, the maximum linear speed – 5.65 cm/s. The probe loads ($F_n$) were preset as 1 N, 2 N, 5 N. To increase the statistics of the test results, nine tribotests were carried out, three at each load. At the maximum load ($F_N$=5 N), using the standard analysis technique [16], based on Hertz's equations [17], and the tabular data on Young's modulus and Poisson's ratio [18-20], the initial (before tribotest) maximum contact pressure value ($P_{Hmax}$) was calculated. For the current tribological test with the 100Cr6 steel ball, the $P_{Hmax}$ value was 1517 MPa. It is known, that the microhardness ($H_V$) of $Ga_2O_3$ layers strongly depends on their structure: some authors report that the values of $H_V$ at room temperature vary from 8 to 20 GPa [7,19]. The calculation (by standard analysis technique [16]) of the maximum shear stress ($\tau_{Hmax}$) that occurs in $Ga_2O_3$ layers ($F_N$=5 N) gave the value of 470 MPa. Based on this, even at the maximum contact pressures, no macroscopic destruction of the layer should happen. Thus, it can be expected, that the shear strain, arising during friction at the interface between the contrbodies, should not change the destruction conditions of the coating material.

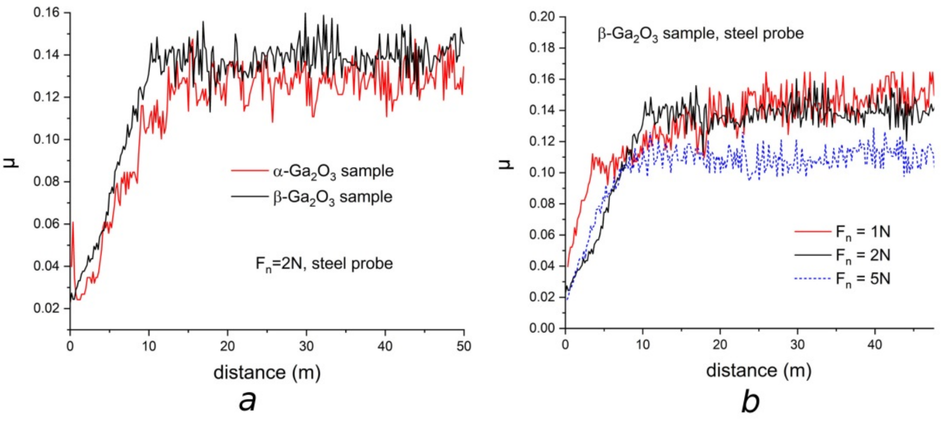

**Fig. 1.** Dependences of COF vs. probe position during tribotest:
a – α- and β- $Ga_2O_3$ layers at $F_N$ = 2N; b – β-$Ga_2O_3$ layer at various loads ($F_N$)

Figure 1 illustrates the results of the tribological experiments. Comparison of the test results for the α- and β-$Ga_2O_3$ layers (each at 2N - load) is depicted in Fig. 1a. One can see that the COF values for the α-phase are lower. The dependences of $\mu$ on the probe position (the total probe run) for various loads $F_N$ obtained during testing the β-$Ga_2O_3$ layers (one of the test sets) see at Fig. 1b. The average COF value decreases with increasing the load. It should be noted that all curves have an initial non-steady region (up to 10 m), where the COF values are low. Finally, the average COF values obtained for $Ga_2O_3$ layers are as follows: μ (β- $Ga_2O_3$) = 0.126 ± 0.026 and μ (α- $Ga_2O_3$) = 0.116 ± 0.024, which are even lower than ones for the gallium nitride (μ (GaN) = 0.21-0.28) and the sapphire (μ (α-$Al_2O_3$) = 0.15-0.20) [21-23].

After the tribological tests were completed, the wear tracks widths (obtained at various loads) of the α- and β- $Ga_2O_3$ samples were scanned and measured by SEM. These wear tracks were (selectively) depicted in Fig. 2. The comparison between the α- and β- $Ga_2O_3$ wear tracks (Fig. 2a and Fig. 2b correspondingly) shows, that the α-phase demonstrates a significantly higher wear resistance at small loads (1 N and 2 N). The wear track of the α-$Ga_2O_3$ is 30 times narrower than the β- $Ga_2O_3$ one at $F_N$=1 N. However, with an increase of the load up to 5 N, the α-phase layer is practically removed, and the wear track width doubled in comparison with the β-phase. It is assumed, that the complete destruction of the α- $Ga_2O_3$ layer abraded by a steel ball at high loads is caused by high stresses exist in heteroepitaxial layers of high crystal quality. The reason for that is a difference in the lattice and thermoelastic constants of layer and substrate. Previously we observed the self-separation of an 8 – 10µm thick α- $Ga_2O_3$ layer during epitaxy runs. Another factor is that the α- $Ga_2O_3$ has higher structural quality than the β- $Ga_2O_3$ one, which was confirmed earlier by their ω-scans: FWHM is 240 arcsec vs. 20 arcmin, α- and β-phase correspondingly [10,11]. All these circumstances activate additional tensions in an interface layer.

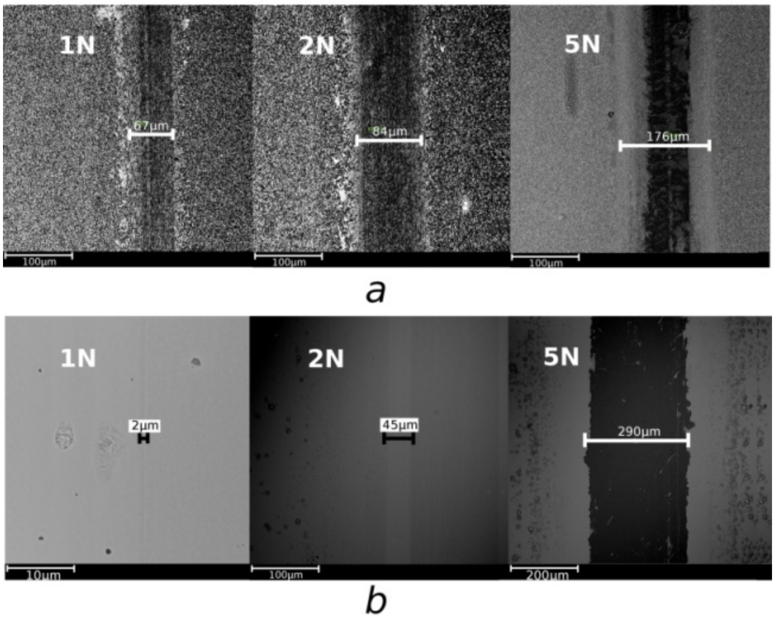

**Fig. 2.** SEM-images of the wear scars obtained by tribological tests:
(a) β-$Ga_2O_3$ and (b) α-$Ga_2O_3$ layers

To calculate the wear coefficients $k$ [$mm^3$/N·m] for the $Ga_2O_3$ layers, the cross-sections (which are perpendicular to the lateral surface and the track axis) of the wear tracks were considered. The profiles were scanned by the profilometer. In Figure 3 a profile of β-$Ga_2O_3$

layer, after the tribotest at $F_N$=2 N is showed as an example. As soon as the areas of the cross-sections.

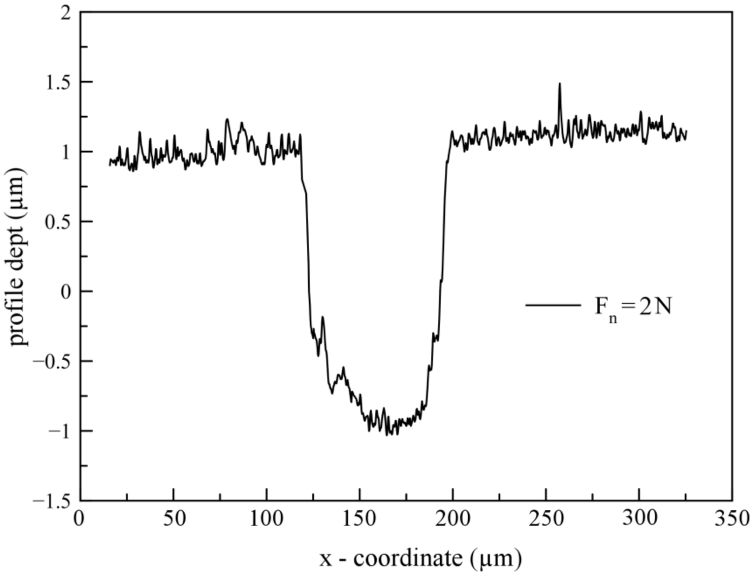

**Fig. 3.** A profile of the β- $Ga_2O_3$ layer (tribotest at $F_N$=2 N)

($S_c$) were calculated, it was found, that their values are almost constant at any position along the certain wear track axis. Assuming that the hardnesses of the $Ga_2O_3$ layers and the 100Cr6 steel ball are close, and the geometry of contact is in all tests is constant, the Archard model can be applied [24]. With help of (1), the wear coefficients ($k$) for the α- and β-$Ga_2O_3$ coatings were calculated:

$$k = \frac{V}{F_n \cdot d} \quad (1),$$

where $d$ – is a total probe run and $V$ – is a volume of the material removed during the complete test. Latter was calculated by multiplying the cross-sectional area by a half-length of the one cycle at the reciprocating test. To facilitate analysis, the values of the wear coefficients were recalculated in terms of the maximum contact pressures ($P_{Hmax}$) [16].

The wear coefficient values at different $P_{Hmax}$ values for both $Ga_2O_3$ layers are presented in Fig. 4. The average values of $k$ for the α-$Ga_2O_3$ layers at small loads are relatively low: $15 \cdot 10^{-7} mm^3/(N \cdot m)$ ($F_N$ = 1 N or $P_{Hmax}$ = 887 MPa) and $50 \cdot 10^{-7} mm^3/(N \cdot m)$ ($F_N$ = 2 N or $P_{Hmax}$ = 1118 MPa). For comparison, the value of $k$ (at ISA) for the diamond layers is predictably lower – $10^{-7}$-$10^{-9} mm^3/(N \cdot m)$, at the same time for GaN and sapphire $k$ values are about $10^{-7}$-$10^{-8}$ $mm^3/(N\ m)$ [21,22], which are close to one obtained in this paper. Despite the fact that the wear coefficient of the β-$Ga_2O_3$ is relatively high ($5 \cdot 10^{-5} mm^3/(N \cdot m)$), generically, this layer still can be considered as a sufficiently wear-resistant one.

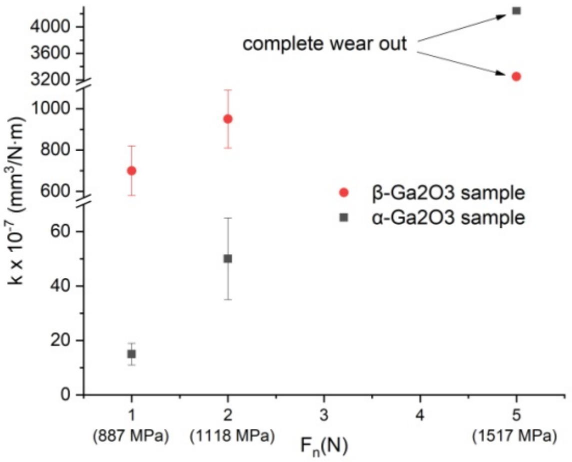

**Fig. 4.** Wear coefficient (k) values for α- and β- $Ga_2O_3$ layers at various loads ($F_N$) and maximum contact pressure values ($P_{Hmax}$)

Presumably, such low COFs obtained for both $Ga_2O_3$ layers can be explained by the formation of an ultrafine powder on the surface of the layers during a friction process. This powder can play a role of a dry lubricant. A similar effect was showcased by the nanodiamond particles that were peeled off the specimen during diamond tribotests [25]. Such nano-powder was capable of lowering the COF to extremely low values of about 0.02. At the same time, the roughness values of the β-$Ga_2O_3$ layers are high, which can explain the increase of the COF compared with one for the α-phase layers. The wear coefficients for both $Ga_2O_3$ polymorphs have relatively low values. However, taking into account the structural anisotropy one can assume that the wear coefficients of some crystal orientations may be lower. For completeness, it will be useful to vary the presets and conditions of the tribological tests, for example, the contrbody material or humidity. This might be a challenge for future investigations in this area.

## 4. Summary

Both (0001) α-$Ga_2O_3$ and ($\bar{2}01$) β-$Ga_2O_3$ layers have appropriate characteristic for wearing application:

1. All specimens have very low COFs: 0.12 and 0.13 for the α- and β-phases respectively, that is approximately 30% lower than the sapphire layer has;
2. Both $Ga_2O_3$ polymorphs have relatively high wear resistance. This especially applies to the α-$Ga_2O_3$ layer. It has a wear coefficient of ~ $10^{-6}$mm$^3$/N·m, which is close to one for the sapphire (~ $10^{-7}$ mm$^3$/N·m).

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